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## III. Researches on Vanadium.—Part III. Preliminary Notice.

By HENRY E. ROSCOE, B.A., F.R.S. Received April 7, 1870.

## I. METALLIC VANADIUM\*.

In the second part of "Researches on Vanadium," it was stated that the metal absorbs hydrogen. This conclusion has been fully borne out by subsequent experiment; and it appears that the amount of absorbed or combined hydrogen taken up by the metal varies according to the state of division, first, of the chloride ( $VCl_3$ ) from which the metal is prepared, and secondly, and especially, of the metal itself. The metal containing absorbed hydrogen slowly takes up oxygen on exposure to dry air, water being formed and the metal undergoing oxidation to the lowest oxide,  $V_2O$ . At this point the oxidation stops, but in moist air it proceeds still further.

The difficulty of obtaining metallic vanadium free from admixture of oxide has been again rendered evident. Perfectly pure tetrachloride was prepared in quantity, and from this pure dichloride was made. On heating this to whiteness in dry hydrogen for 48 hours a substance was obtained which gained on oxidation 70·7 per cent. (vanadium requiring 77·79 per cent. increase), and therefore still contained a slight admixture of oxide.

The reducing action of sodium on the solid chlorides was next examined; in this case the reduction takes place quietly in an atmosphere of hydrogen at a red heat, and is best conducted in strong iron tubes. Explosions occur when sodium acts on the liquid tetrachloride. The substance thus obtained was found, after lixiviation, to be free from chlorine, and on washing it separated into two portions—(1) a light and finely divided black powder (trioxide), which remains in suspension, and is soluble in hydrochloric acid, and (2) a heavier grey powder, insoluble in hydrochloric acid, which soon deposits, and can, by repeated washing, be completely freed from the lighter trioxide. This bright grey powder consists of metallic vanadium, mixed with more or less oxide. If this metallic powder, after drying *in vacuô*, be reduced at a low red heat in a current of pure hydrogen, it takes fire spontaneously, even when cold, on exposure to air or oxygen, water being formed, whilst the vanadium undergoes oxidation, forming the blue oxide,  $V_2O_4$ . A portion of metal exposed for some weeks to the air also slowly absorbed oxygen, passing into the oxide,  $V_2O$ .

## II. VANADIUM AND BROMINE.

1. *Vanadium Tribromide*,  $VBr_3$ , molec. wt. = 291·3.—When excess of bromine is passed over vanadium mononitride heated to redness, a vivid action occurs, and dense dark-brown vapours are formed, condensing in the cooler portions of the tube to a greyish-black, opaque, amorphous mass of the tribromide. The tribromide is a very unstable compound, losing bro-

\* Phil. Trans. 1869, p. 679.

mine even when kept sealed up in glass tubes; it is very deliquescent, and on heating in the air rapidly loses all its bromine and takes up oxygen, with formation of vanadic acid. On being thrown into water, the tribromide readily dissolves, forming a brown liquid (in this respect resembling the trichloride), which, on addition of a few drops of hydrochloric acid, turns of a bright green colour, showing the presence of a solution of an hypovanadic salt. No free bromine or hydrobromic acid is given off on dissolving the tribromide in water. That a more volatile higher bromide was not formed in this reaction was shown, inasmuch as, on distilling the excess of liquid which had collected in the receiver, it was found to consist of free bromine, containing mere traces of the tribromide mechanically carried over. The tribromide is likewise formed when bromine is passed over a red-hot mixture of vanadium trioxide and pure charcoal, as in the preparation of the tetrachloride; but this method is not one to be recommended, as the tube becomes constantly stopped up by the formation of the solid tribromide.

The analysis of the tribromide was made by dissolving the compound in water, and precipitating the bromine with excess of nitrate of silver, the vanadium being estimated as  $V_2O_5$ , either in the filtrate from the bromide of silver or in a separate portion. The bromine in the above determinations, obtained by precipitation as silver-salt, was invariably found to be too high, whilst the vanadium nearly agreed with the theoretical percentage. This is due to the fact pointed out by Stas, in his '*Recherches*,' p. 156, that bromide of silver, when boiled, encloses mechanically a portion of the precipitant, which then cannot be washed out. The loss of weight obtained by reducing the bromide to metallic silver in a current of hydrogen, taken as bromine, gave more nearly agreeing numbers:—

		Calculated.	Mean of 6 determinations.
Vanadium.... V	= 51.3	17.61	18.44
			Mean of 3 determinations.
Bromine .... Br <sub>3</sub>	= 240.0	82.39	80.86
	291.3	100.00	99.30

2. *Vanadium Oxytribromide*, or *Vanadyl Tribromide*,  $VOBr_3$ , molec. wt. = 307.3.—The oxytribromide is a dark-red transparent liquid, evolving white fumes on contact with the air, obtained by passing pure and dry bromine over vanadium trioxide ( $V_2O_5$ ) heated to redness. Moisture prevents the formation of the oxytribromide; and it not only undergoes sudden decomposition when heated to  $180^\circ$ , but also slowly decomposes at the ordinary atmospheric temperatures. The boiling-point of the tribromide can, however, be brought below its temperature of decomposition by distillation *in vacuô*, and the liquid can then be freed completely from bromine by passing a current of dry air through the liquid. Under a pressure of 100 millims. the oxytribromide boils from  $130^\circ$  to  $135^\circ$ , and may be

distilled almost without decomposition. Vanadium oxytribromide dissolves in water, yielding a yellow-coloured solution, in which both vanadium and bromine were determined, after reduction with sulphurous acid :—

	Calculated.	Mean of several analyses.
V ..... = 51·3	16·69	16·75
Br <sub>3</sub> ..... = 240·0	78·10	79·20
O ..... = 16·0	5·21	—
	<hr/>	<hr/>
307·3	100·00	

The specific gravity of the oxytribromide at 0° is 2·967.

3. *Vanadium Oxydibromide*, or *Vanadyl Dibromide*,  $\text{VOBr}_2$ , molec. wt. = 227·3.—This is a solid substance, of a yellowish-brown colour, obtained by the sudden decomposition of the foregoing compound at temperatures above 100°, or by its slow decomposition at the ordinary temperature.

The oxydibromide is very deliquescent, dissolving in water, with formation of a blue solution of a vanadious salt. When heated in the air it loses all its bromine, and is converted into  $\text{V}_2\text{O}_5$ .

Analysis gave :—

	Calculated.	Mean of several analyses.
V ..... = 51·3	22·57	22·45
Br <sub>2</sub> ..... = 160·0	70·39	70·93
O ..... = 16·0	7·104	—
	<hr/>	<hr/>
227·3	100·00	

### III. VANADIUM AND IODINE.

Iodine-vapour does not attack either the trioxide or the nitride at red heat; both these substances remain unchanged, and no trace of vanadium can be detected in the iodine which has passed over them.

### IV. THE METALLIC VANADATES.

In the first part of these Researches (Phil. Trans. 1868) it was pointed out (1) that the salts analyzed by Berzelius must be considered as meta- or monobasic vanadates, (2) that the so-called bivanadates analyzed by Von Hauser are anhydro-salts, and (3) that the ortho- or tribasic vanadates contain 3 atoms of monad metal, the sodium salt being formed artificially by fusing 1 molecule of vanadium pentoxide with 3 molecules of carbonate of soda, when 3 molecules of carbon dioxide are expelled, whilst the ortho-salts occur native in many minerals. The present communication contains a description of these classes of salts, as well as of a new class of salts, the tetrabasic or pyro-vanadates.

*Sodium Vanadates.*

1. *Ortho- or Tri-Sodium Vanadate*,  $\text{Na}_3\text{VO}_4 + 16\text{H}_2\text{O}_2$ .—When a mixture of 3 molecules of  $\text{Na}_2\text{CO}_3$  and 1 molecule of  $\text{V}_2\text{O}_5$  is fused until no

further evolution of  $\text{CO}_2$  is observed, a tribasic vanadate remains as a white crystalline mass. This mass dissolves easily in water, and on addition of absolute alcohol to the solution two layers of liquid are formed; the lower one solidifies after a time, forming an aggregation of needle-shaped crystals, which possess a strongly alkaline reaction. These having been washed with alcohol, and dried on a porous plate over sulphuric acid *in vacuo*, were analyzed with the following results:—

	Calculated.	Found.
$\text{Na}_3$ . . . . . = 69.0	14.6	13.8
V . . . . . = 51.3	10.86	10.86
$\text{O}_4$ . . . . . = 64.0	13.56	—
$16\text{H}_2\text{O}$ . . . . . = 288.0	60.97	60.44
	<hr/> 472.3	<hr/> 99.99

The sodium in this and in the following compounds was separated from the vanadium by precipitating the vanadic acid as the perfectly insoluble basic lead salt hereafter described. This was dried at  $100^\circ$  and weighed, then dissolved in nitric acid and decomposed by sulphuric acid, and the solution of  $\text{V}_2\text{O}_5$  in excess of this acid gave on evaporation a finely crystalline mass. The filtrate from the lead precipitate freed from lead yielded on evaporation sodium sulphate. Full analytical details of this method, as well as of the other by precipitation as the insoluble ammonium metavanadate, are given in the memoir. By frequent crystallizations the trisodium vanadate is slowly decomposed into the tetrasodium salt, caustic soda being formed. This singular reaction was most carefully examined and the amount of sodium hydroxide liberated determined volumetrically.

2. *Tetrasodium Vanadate*,  $\text{Na}_4\text{V}_2\text{O}_7 + 18\text{H}_2\text{O}$ .—This salt crystallizes in beautiful six-sided tables; it is easily soluble in water, insoluble in alcohol, and is precipitated by the latter liquid from aqueous solution in white scales of a silky lustre. As long as the salt contains free alkali or tribasic salt, it forms, on precipitation with alcohol, oily drops which solidify after some time. The tetrasodium vanadate is always formed by the first fusion of vanadic acid with excess of carbonate of soda, and can be easily prepared in the pure state by recrystallization.

	Calculated.	Found (mean of many determinations).
$\text{Na}_4$ . . . . . = 92.0	14.58	14.61
$\text{V}_2$ . . . . . = 102.6	16.27	15.97
$\text{O}_7$ . . . . . = 112.0	17.27	—
$18\text{H}_2\text{O}$ . . . . = 324.0	51.38	51.80
	<hr/> 630.6	<hr/> 99.99

The salt loses 17 molecules of water at  $100^\circ$ .

The corresponding Calcium and Barium Vanadates,  $\text{Ca}_2\text{V}_2\text{O}_7$ , and  $\text{Ba}_2\text{V}_2\text{O}_7$ , are white precipitates obtained by adding the chlorides to a

solution of tetrasodium vanadate. If calcium chloride be added to a solution of the trisodium salt, dicalcium vanadate is precipitated, the solution becoming strongly alkaline from formation of calcium hydroxide and absorbing carbonic acid from the air. Complete analysis showed that the calcium salt contains  $2\frac{1}{2}$  molecules of water of crystallization, whilst the barium salt is anhydrous.

### Lead Vanadates.

1. *Tribasic or Ortho-Lead Vanadate*,  $Pb_3 2(VO_4)$ .—Obtained as a light yellow insoluble powder on precipitating the tribasic sodium salt with a soluble lead salt; it yielded on analysis 11.75 per cent. of vanadium, the calculated quantity being 12.04 per cent.

2. *Vanadinite, the Double Orthovanadate and Chloride of Lead*,  $3Pb_3 VO_4 + Pb Cl_2$ , can be artificially prepared by fusing for a few hours a mixture of vanadic acid, oxide of lead, and chloride of lead, in the above proportions, together with an excess of sodium chloride. After cooling, a greyish crystalline mass is left, containing cavities filled with long crystals having the same colour as the mass, which under the microscope could be distinguished as six-sided prisms. The crystalline powder is then boiled with water until no further traces of soluble chlorides are extracted.

The following analysis shows that this substance has the same composition as the vanadinites from Zimapan and Windischkappel, analyzed by Berzelius and Rammelsberg\* :—

	Calculated. 3 ( $Pb_3 VO_4$ ) Pb $Cl_2$ .	Natural vanadinite.		Artificial vanadinite.
		Zimapan, Berzelius.	Windischkappel, Rammelsberg.	
Lead . . . . .	73.08	70.4	71.20	71.96
Vanadium . . . .	10.86	—	9.77	11.11
Chlorine . . . .	2.50	2.54	2.23	2.31
Oxygen . . . . .	13.55	—	—	—

The specific gravity of the artificial vanadinite at 12° C. is 6.707, that of the natural being 6.886.

3. *Basic Di-Lead Vanadate*,  $2(Pb_2 V_2 O_7) + Pb O$ .—This salt is precipitated as a pale yellow powder when acetate of lead is added to a solution of disodium vanadate, the liquid acquiring an acid reaction. It is completely insoluble in water and in dilute acetic acid, but dissolves readily in nitric acid.

	Calculated.	Mean found.
$Pb_5$ . . . . . =	1035.0	69.92
$V_4$ . . . . . =	205.2	13.86
$O_{15}$ . . . . . =	240.0	16.22
	1480.2	70.18
		13.3

\* Pyromorphite and apatite have already been artificially prepared by Deville and Caron, and also by Debray, whilst mimetosite has been obtained artificially by Lechartier.

*Silver Vanadates.*

1. *The Ortho-Silver Vanadate*,  $\text{Ag}_3\text{VO}_4$ , is obtained as an orange-coloured precipitate by mixing a freshly prepared solution of the trisodium salt with a solution of silver nitrate, in which every trace of free acid has been neutralized; unless these precautions are attended to, the precipitate consists of a mixture of the ortho- and pyro-salt. The trisilver vanadate is insoluble in water, but readily dissolves in ammonia and nitric acid. Analysis gave the following results:—

	Calculated.	Found (mean).
$\text{Ag}_3$ . . . . . = 324.0	73.75	73.83
V . . . . . = 51.3	11.67	11.76
$\text{O}_4$ . . . . . = 64.0	14.58	—
	<hr/> 439.3	<hr/> 100.00

2. *The Tetrabasic Silver Vanadate*,  $\text{Ag}_4\text{P}_2\text{O}_7$ , is prepared by mixing a solution of the corresponding sodium salt with a neutral solution of nitrate of silver. It falls as a yellow dense crystalline precipitate, resembling in colour the ordinary phosphate of silver. On dissolving the salt in nitric acid, the silver is precipitated as chloride, and the vanadium determined as  $\text{V}_2\text{O}_5$ .

Analysis gave:—

	Calculated.	Found.
$\text{Ag}_4$ . . . . . = 432	66.81	66.45
$\text{V}_2$ . . . . . = 102.6	15.87	15.97
$\text{O}_7$ . . . . . = 112.0	17.32	—
	<hr/> 646.6	<hr/> 100.00

The reactions of the tri- and tetrabasic vanadates of the other metals are then described.

The author has to thank Messrs. Oelhofer and Finkelstein for the valuable assistance which they have given him in the above investigation.

The Society adjourned over the Easter Recess to Thursday, April 28.

*April 28, 1870.*

Dr. WILLIAM ALLEN MILLER, Treasurer and Vice-President,  
in the Chair.

Principal Dawson, LL.D., of McGill College, Montreal, was admitted into the Society.

The following communications were read:—